DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the electrolytic solution and a rechargeable battery. It is related with the electrolytic solution used for the rechargeable battery and it whose safety under a overcharge situation improved in detail.
[0002]
[Description of the Prior Art] For example, the electrolytic solution which dissolved lithium salt in the solvent which makes nonaqueous solvents, such as a carbonate, the ether, and lactone, a subject as the electrolytic solution for lithium secondary batteries is known. These nonaqueous solvents are solvents which were excellent highly [a dielectric constant] on cell properties, such as excelling also in the stability at the time of cell use since oxidation potential is high.
[0003] On the other hand, although use with potential high for the Takayasu quality of this nonaqueous solvent is possible for the electrolytic solution using the above nonaqueous solvents therefore, the so-called overcharge phenomenon which becomes an electrical potential difference more than a predetermined upper limit electrical potential difference at the time of charge etc. tends to pose a problem conversely. Since phenomena, such as ignition and a burst, can also be caused not only deformation and generation of heat of a cell but when excessive if it is overcharged, it is important to raise the safety of the rechargeable battery at the time of overcharge.
[0004] Although lithium transition-metals multiple oxides which have the layer structure, such as lithium cobalt oxide ($LiCoO_2$) and a lithium nickel oxide ($LiNiO_2$), are especially mentioned as a leading ingredient as positive active material of a lithium secondary battery since the capacity per weight is large Since these compounds will be in the condition that the lithium ion almost ****ed in the overcharge condition, and become unstable, the electrolytic solution and rapid exothermic reaction may be caused or a lithium metal may be deposited on a negative electrode, the safety at the time of overcharge is very important.
[0005] As an attempt which raises the safety at the time of such overcharge conventionally, a overcharge inhibitor is added in the electrolytic solution and the approach of intercepting a current is learned. That is, when aromatic compounds, such as a biphenyl which has the oxidation potential beyond the upper limit electrical-potential-difference value of a cell, are added in the electrolytic solution as a overcharge inhibitor, and it changes into a overcharge condition, and the above-mentioned aromatic compound carries out an oxidation polymerization and forms the coat of high resistance in an active material front face, it is the approach of suppressing a overcharge current and stopping advance of overcharge (for example, each official report of JP,9-106835,A, patent No. 2939469, and patent No. 2983205 etc.).
[0006]
[Problem(s) to be Solved by the Invention] However, the present condition was being unable to say that the above-mentioned overcharge prevention approach is also enough. For example, since the terphenyl derivative which is the overcharge inhibitor which the biphenyl which is the overcharge inhibitor indicated by JP,9-106835,A, 3-chloro thiophene, a furan, etc. may have a bad influence on a cell property, and was indicated by the patent No. 2939469 official report had the low solubility to the electrolytic solution, the diphenyl ether which is the overcharge inhibitor which may bring about cell performance degradation and was further indicated by the patent No. 2983205 official report had the trouble it was strong and were hard to treat an irritating odor.
[0007] Then, the new overcharge inhibitor which has sufficient overcharge prevention effectiveness was called for.
[0008]
[Means for Solving the Problem] This invention is made in view of the above-mentioned trouble, and the purpose aims

at prevention of the overcharge which was more excellent using the effective overcharge inhibitor, and is to raise the safety at the time of overcharge. As a result of repeating examination wholeheartedly that this invention persons should attain the above-mentioned purpose, as a overcharge inhibitor Although the dicarboxylic acid diester (however, oxalic acid diester and succinic-acid diester remove) which is not the compound of the conventional aromatic series system, and its derivative are strong to oxidation, they can use it as a overcharge inhibitor, And based on a header and its knowledge, this invention was completed for the safety at the time of sufficient overcharge being securable by using said comparatively little dicarboxylic acid diester or its derivative to the solvent which makes nonaqueous solvents, such as a carbonate, the ether, and lactone, a subject.

[0009] That is, the summary of this invention consists in the electrolytic solution characterized by containing dicarboxylic acid diester (however, oxalic acid diester and succinic-acid diester being removed) and its derivative 0.1 to 5% of the weight to the above-mentioned solvent in the electrolytic solution which comes to dissolve lithium salt in the solvent which makes a subject at least one sort of nonaqueous solvents chosen from the group which consists of a carbonate, the ether, and lactone.

[0010] Other summaries of this invention consist in the rechargeable battery characterized by having the above-mentioned electrolytic solution, a positive electrode, and a negative electrode.

[0011]

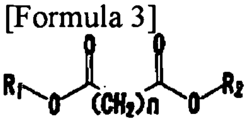
[Embodiment of the Invention] Hereafter, it explains to a detail about the operation gestalt of this invention. The solvent used for the electrolytic solution of this invention makes a subject at least one sort of nonaqueous solvents chosen from the group which consists of a carbonate, the ether, and lactone. the content rate of these nonaqueous solvents -- the solvent whole -- receiving -- usually -- it takes still more preferably for 100 % of the weight more than 80% weight preferably 50% of the weight or more. When there are too few rates that the above-mentioned nonaqueous solvent occupies, the trouble that degradation accompanying the fall of the electrical conductivity of the electrolytic solution etc. and the oxidation reduction reaction of the electrolytic solution is large may arise.

[0012] As a carbonate which can be used as the above-mentioned nonaqueous solvent, chain-like carbonates, such as annular carbonates, such as propylene carbonate (PC) and ethylene carbonate (EC), dimethyl carbonate (DMC), diethyl carbonate (DEC), and ethyl methyl carbonate (EMC), etc. can be illustrated. Moreover, dimethoxyethane (DME), diethoxy-ethane (DEE), etc. can be illustrated as the ether which can be used as the above-mentioned nonaqueous solvent.

[0013] Moreover, gamma-butyrolactone (GBL), gamma-valerolactone, etc. can be illustrated as lactone which can be used as the above-mentioned nonaqueous solvent. Although at least one sort of a carbonate, the ether, and lactone should just be used for the above-mentioned nonaqueous solvent, it makes a carbonate contain preferably. Of course, two or more of these sorts can also be used together. Especially a desirable thing is a mixed solvent with the lactone which are high dielectric constant solvents, such as annular carbonates, such as PC and EC, or GBL, and chain-like carbonates, such as DMC, DEC, EMC, etc. which are a hypoviscosity solvent.

[0014] In this invention, it is characterized by making dicarboxylic acid diester (however, oxalic acid diester and succinic-acid diester being removed) and its derivative contain 0.1 to 5% of the weight as a overcharge inhibitor in the electrolytic solution. Dicarboxylic acid dialkyl ester is used preferably as this dicarboxylic acid diester. As a compound suitable as the above-mentioned dicarboxylic acid diester, it is following general formula (1): [0015].

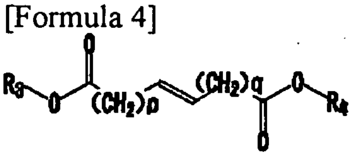
[Formula 3]



(1)

[0016] (-- R1 and R2 express the alkyl group or halogenation alkyl group of carbon numbers 1-10 among a formula, and n is the integer of 1, and 3-10.) -- the saturation dicarboxylic acid diester expressed and following general formula (2): [0017]

[Formula 4]



(2)

[0018] (-- R3 and R4 express the alkyl group or halogenation alkyl group of carbon numbers 1-10 among a formula, and p and q are the integers of 0-5, respectively, and are 0 <=p+q<=10.) -- partial saturation dicarboxylic acid diester ** expressed is mentioned. R1, R2, R3, and R4 in the above-mentioned general formula (1) and (2) are the alkyl group

or halogenation alkyl group of carbon numbers 1-10. Specifically A methyl group, an ethyl group, a propyl group, an isopropyl group, butyl, An isobutyl radical, s-butyl, t-butyl, a pentyl radical, an isopentyl radical, A neopentyl radical, a hexyl group, a heptyl radical, an octyl radical, a nonyl radical, A decyl group, a fluoro methyl group, difluoromethyl group, a trifluoromethyl radical, A trifluoroethyl radical, a pentafluoro propyl group, a trifluoroethyl radical, Heptafluoro butyl, a nona fluoro pentyl radical, a tetrafluoro propyl group, Hexafluoro butyl, an octafluoropentyl radical, a propyl fluoro methyl group, Propyl difluoromethyl group, a propyl trifluoromethyl radical, a butyl fluoro methyl group, butyl difluoromethyl group, a butyl trifluoromethyl radical, a pentafluorobutyl radical, a heptafluoro pentyl radical, etc. can be mentioned. Moreover, n in the above-mentioned general formula (1) is the integer of 1, and 3-10, and p and q in a general formula (2) are the integer of 0-5, respectively, and fill the relational expression of 0 <=p+q<=10. Since it is in the inclination for the solubility over said solvent to fall when the carbon number of the above R1-R4, n, and p+q exceed 10, there is a possibility that the overcharge prevention effectiveness may fall.

[0019] If it is a compound with the molecule frame of dicarboxylic acid diester as the above-mentioned dicarboxylic acid diester, except for oxalic acid diester and succinic-acid diester, it will not be limited especially. Moreover, these derivatives can also be used. As a derivative, various kinds of compounds which have the above-mentioned dicarboxylic acid diester frame, such as what permuted a part of hydrogen atom of the above-mentioned dicarboxylic acid diester in the substituent, can be mentioned. As the above-mentioned substituent, for example A halogen atom, an oxygen atom, a sulfur atom, The amino group, an alkylamino radical, an arylamino radical, the carvone amino group, A sulfonamide radical, an oxy-carbonyl-amino radical, an oxy-sulfonylamino radical, An ureido radical, hydroxyl, a sulfhydryl group, a methoxyl group, the low-grade alkyl group of carbon numbers 1-3, A cycloalkyl radical, an alkoxy group, an alkenyl radical, an alkynyl group, an aralkyl radical, An aryl group, a cyano group, a nitro group, a formyl group, an aryloxy group, An alkylthio group, an acrylic radical, an aryl thio radical, an acyloxy radical, a sulfonyloxy radical, An acyl group, an oxy-carbonyl group, a carbamoyl group, a sulfonyl group, a sulfinyl group, An oxy-sulfinyl group, a sulfamoyl group, a carboxylic-acid radical or its salt, a sulfonic group or its salt, a phosphonic acid radical or its salt, heterocycle residue, or a hydroxyl group can be mentioned. In addition, the carbon number of the above-mentioned substituent is usually five or less preferably ten or less.

[0020] As an example of the dicarboxylic acid diester to be used and its derivative Dimethyl malonate, a diethyl malonate, malonic-acid dipropyl, dibutyl malonate, A malonic-acid screw (fluoro methyl), a malonic-acid screw (difluoromethyl), Malonic-acid diester, such as a malonic-acid screw (trifluoromethyl), maleic-acid dimethyl, A diethyl maleate, maleic-acid dipropyl, dibutyl maleate, A maleic-acid screw (fluoro methyl), a maleic-acid screw (difluoromethyl), Diester maleate, such as a maleic-acid screw (trifluoromethyl), Dimethyl fumarate, diethyl fumarate, fumaric-acid dipropyl, fumaric-acid dibutyl, A fumaric-acid screw (fluoro methyl), a fumaric-acid screw (difluoromethyl), Fumarate diester, such as a fumaric-acid screw (trifluoromethyl), glutaric-acid dimethyl, Glutaric-acid diethyl, glutaric-acid dipropyl, glutaric-acid dibutyl, A glutaric-acid screw (fluoro methyl), a glutaric-acid screw (difluoromethyl), Glutaric-acid diester, such as a glutaric-acid screw (trifluoromethyl), Adipic-acid dimethyl, adipic-acid diethyl, adipic-acid dipropyl, Adipic-acid dibutyl, bis adipate (fluoro methyl), bis adipate (difluoromethyl), Di-ester adipate, such as bis adipate (trifluoromethyl), Pimelic-acid dimethyl, pimelic-acid diethyl, a pimelic-acid screw (fluoro methyl), Pimelic-acid diester, such as a pimelic-acid screw (difluoromethyl) and a pimelic-acid screw (trifluoromethyl), Suberic-acid dimethyl, suberic-acid diethyl, suberic-acid dipropyl, Suberic-acid dibutyl, a suberic-acid screw (fluoro methyl), a suberic-acid screw (difluoromethyl), Suberic-acid diester, such as a suberic-acid screw (trifluoromethyl), Azelaic-acid dimethyl, azelaic-acid diethyl, azelaic-acid dipropyl, Azelaic-acid dibutyl, an azelaic-acid screw (fluoro methyl), an azelaic-acid screw (difluoromethyl), Azelaic-acid diester, such as an azelaic-acid screw (trifluoromethyl), Dimethyl sebacate, sebacic-acid diethyl, sebacic-acid dipropyl, A dibutyl sebacate, a sebacic-acid screw (fluoro methyl), a sebacic-acid screw (difluoromethyl), Sebacic-acid diester, such as a sebacic-acid screw (trifluoromethyl), Undecane diacid dimethyl, undecane diacid diethyl, undecane diacid dipropyl, Undecane diacid dibutyl, an undecane diacid screw (fluoro methyl), Undecane diacid diester, such as an undecane diacid screw (difluoromethyl) and an undecane diacid screw (trifluoromethyl), Dodecane diacid dimethyl, dodecane diacid diethyl, dodecane diacid dipropyl, Although dodecane diacid diester, such as dodecane diacid dibutyl, a dodecane diacid screw (fluoro methyl), a dodecane diacid screw (difluoromethyl), and a dodecane diacid screw (trifluoromethyl), acetone-dicarboxylic acid diethyl, etc. can be mentioned, it is not limited to these. Especially, dimethyl malonate, a diethyl malonate, malonic-acid dipropyl, Dibutyl malonate, a malonic-acid screw (fluoro methyl), a malonic-acid screw (difluoromethyl), Malonic-acid diester, such as a malonic-acid screw (trifluoromethyl), maleic-acid dimethyl, A diethyl maleate, maleic-acid dipropyl, dibutyl maleate, A maleic-acid screw (fluoro methyl), a maleic-acid screw (difluoromethyl), Diester maleate, such as a maleic-acid screw (trifluoromethyl), Dimethyl fumarate, diethyl fumarate, fumaric-acid dipropyl, fumaric-acid dibutyl, A fumaric-acid screw (fluoro methyl), a fumaric-acid screw

(difluoromethyl), Fumarate diester, such as a fumaric-acid screw (trifluoromethyl), glutaric-acid dimethyl, Glutaric-acid diethyl, glutaric-acid dipropyl, glutaric-acid dibutyl, A glutaric-acid screw (fluoro methyl), a glutaric-acid screw (difluoromethyl), Glutaric-acid diester, such as a glutaric-acid screw (trifluoromethyl), is desirable. Still more preferably Dimethyl malonate, a diethyl malonate, malonic-acid dipropyl, Dibutyl malonate, a malonic-acid screw (fluoro methyl), a malonic-acid screw (difluoromethyl), Malonic-acid diester, such as a malonic-acid screw (trifluoromethyl), maleic-acid dimethyl, A diethyl maleate, maleic-acid dipropyl, dibutyl maleate, A maleic-acid screw (fluoro methyl), a maleic-acid screw (difluoromethyl), Diester maleate, such as a maleic-acid screw (trifluoromethyl), Dimethyl fumarate, diethyl fumarate, fumaric-acid dipropyl, fumaric-acid dibutyl, A fumaric-acid screw (fluoro methyl), a fumaric-acid screw (difluoromethyl), It is fumarate diester, such as a fumaric-acid screw (trifluoromethyl). It is malonic-acid diester, such as dimethyl malonate, a diethyl malonate, malonic-acid dipropyl, dibutyl malonate, a malonic-acid screw (fluoro methyl), a malonic-acid screw (difluoromethyl), and a malonic-acid screw (trifluoromethyl), most preferably. Of course, the derivative of these concrete compounds can be used preferably similarly.

[0021] As for the dicarboxylic acid diester to be used and its derivative, what is dissolved in the above-mentioned nonaqueous solvent is desirable. When solubility is too low, the problem that the effective addition for acting as a overcharge inhibitor is not obtained may arise. Moreover, when the boiling point usually has the too low preferably boiling point which is 120 degrees C or more 100 degrees C or more, it may volatilize inside a cell, and bulging may arise at the time of cell use, or the trouble of not acting effectively as an additive may arise.

[0022] Of course, the dicarboxylic acid diester to be used and its derivative can use two or more sorts together. Although the content of dicarboxylic acid diester and its derivative is made into 5 or less % of the weight to said solvent, it is preferably made into 2 or less % of the weight still more preferably 3 or less % of the weight. When there are too many contents, the trouble of having a bad influence on a cell property may arise. However, since it may not act effectively as a overcharge inhibitor if there are too few contents, it takes still more preferably for 0.5 % of the weight or more 0.25% of the weight or more preferably 0.1% of the weight or more.

[0023] Although these compounds are not clear about the reason for having the overcharge prevention effectiveness by little addition, Li metal and dicarboxylic acid diester which were probably generated to the negative electrode at the time of overcharge reacted within the cell, and it is guessed that advance of overcharge is that of pile stop ******. The electrolytic solution of this invention contains lithium salt in the above-mentioned solvent. As lithium salt, LiClO4, LiAsF6, LiPF6, LiBF4, LiB (C6H5)4, LiCl, LiBr, LiCH3SO3, LiCF3SO3, LiN (SO2CF3)2, LiN (SO2C2F5)2 and LiC (SO2CF3)3, and LiN(SO3CF3)2 grade can be mentioned. Of course, two or more sorts may be mixed and these may be used. Also in the above, it is desirable to use LiBF4 and LiPF6. 0.5-1.5 mols / of concentration of lithium salt are [l.] usually 0.75-1.25 mols/l. preferably to the whole electrolytic solution. Even if lithium salt concentration is too high and it is too low, the fall of electric conductivity may occur, and a bad influence may be in a cell property.

[0024] The electrolytic solution can contain the component of further others if needed. As other components, various kinds of additives and surfactants for forming a coat (SEI) in the active material front face of a cell can be mentioned, for example. The electrolytic solution of this invention can be used for rechargeable batteries, such as a lithium secondary battery. The rechargeable battery of this invention is constituted including a positive electrode, a negative electrode, and said electrolytic solution. Although used as a component of the electrolyte layer between a positive electrode and a negative electrode, as long as said electrolytic solution can raise the safety at the time of overcharge, it may usually be used anywhere in a cell.

[0025] As an active material of the positive electrode which constitutes the rechargeable battery of this invention, a lithium transition-metals multiple oxide is used preferably. As a lithium transition-metals multiple oxide, although the lithium cobalt multiple oxide of LiCoO2 grade, the lithium nickel complex oxide of LiNiO2 grade, the lithium manganese multiple oxide of LiMn2O4 grade, etc. can be mentioned, this invention is effective, when using the lithium transition-metals multiple oxide of a cobalt system and a nickel system with a large lithium content as an active material of a positive electrode, i.e., a lithium cobalt multiple oxide, and lithium nickel complex oxide especially.

[0026] These lithiums transition-metals multiple oxide can also be stabilized by replacing some transition-metals elements which serve as a subject by other metal specieses, such as aluminum, Ti, V, Cr, Mn, Fe, Co, Li, nickel, Cu, Zn, Mg, Ga, and Zr, and is desirable. Of course, two or more sorts of active materials of a positive electrode can also be used together. As an active material of the negative electrode which constitutes the rechargeable battery of this invention, although occlusion and the matter which may be emitted can be used for a lithium, a carbonaceous object is desirable. As an example of this carbonaceous object, the pyrolysis object of the organic substance in various pyrolysis conditions, an artificial graphite, a natural graphite, etc. are mentioned, for example. The ingredient which performed various surface treatment which contains other artificial graphite and purification natural graphites, such as a

graphitization mesophase microsphere and a graphitization mesophase pitch based carbon fiber, in the artificial-graphite list manufactured by elevated-temperature heat treatment of the easy graphite pitch suitably obtained from various raw materials, and contains a pitch in these graphites is used. These carbonaceous objects have that desirable whose d value (distance between layers) of the lattice plane (002nd page) for which it asked by the X diffraction by Gakushin method is 0.335-0.34nm, and what is 0.335-0.337nm is more desirable. It is desirable that it is 1 or less % of the weight, as for ash content, it is more desirable that it is 0.5 or less % of the weight, and it is desirable that it is especially 0.1 or less % of the weight. Moreover, it is desirable that the microcrystal size (Lc) for which it asked by the X diffraction by Gakushin method is 30nm or more, it is more desirable that it is 50nm or more, and it is desirable that it is especially 100nm or more. It can mix in these carbonaceous objects further, and other active materials which can emit [occlusion and] a lithium can also be used for them. As an active material which can emit [occlusion and] lithiums other than a carbonaceous object, metallic-oxide ingredients, such as tin oxide and oxidization silicon, and the lithium alloy of versatility [list / lithium metal] further can be illustrated. Two or more kinds may be mixed and these negative-electrode ingredients may be used.

[0027] The above-mentioned positive electrode and a negative electrode usually contain an above-mentioned active material and an above-mentioned binder, respectively. As a binder, polyvinylidene fluoride, polytetrafluoroethylene, styrene-butadiene rubber, polyisoprene rubber, butadiene rubber, etc. can be mentioned. Furthermore the need can be accepted and electric conduction material, such as carbon materials, such as metallic materials, such as copper and nickel, graphite, and carbon black, can also be made to contain in an electrode. About especially a positive electrode, it is desirable to make electric conduction material contain.

[0028] It is not limited especially about the method of manufacturing an electrode. For example, a binder, a thickener, electric conduction material, a solvent, etc. are added to an active material if needed, and it considers as the shape of a slurry, it can apply to the substrate of a charge collector, and can manufacture by drying, and roll forming of this active material is carried out as it is, and it can consider as a sheet electrode or can also consider as a pellet electrode with compression molding. As a thickener, a carboxymethyl cellulose, methyl cellulose, a hydroxymethyl cellulose, ethyl cellulose, polyvinyl alcohol, oxidization starch, phosphorylation starch, casein, etc. are mentioned.

[0029] as the charge collector which can be used for an electrode -- as a negative-electrode charge collector -- metals, such as copper, nickel, and stainless steel, or an alloy -- desirable -- copper -- it can mention -- moreover -- as a positive-electrode charge collector -- metals, such as aluminum, titanium, and a tantalum, or an alloy -- aluminum and its alloy can be mentioned preferably. In a rechargeable battery, a separator is usually infixed between a positive electrode and a negative electrode. Although not limited especially about the quality of the material or the configuration of a separator to be used, it is stable to the electrolytic solution and it is desirable as a solution retention outstanding ingredient to use a porous sheet or a nonwoven fabric etc. which uses polyolefines, such as polyethylene and polypropylene, as a raw material.

[0030] Especially about the method of manufacturing the nonaqueous rechargeable battery concerning this invention which has a negative electrode, a positive electrode, and a nonaqueous electolyte at least, it is not limited but can choose suitably from the approaches usually adopted. Moreover, the coin type which carried out the laminating of the cylinder type, pellet electrode, and separator of the inside-out configuration which combined the cylinder type, pellet electrode, and separator which were not limited especially about the configuration of a cell but made the sheet electrode and the separator the shape of a spiral is usable.

[0031]

[Example] Hereafter, although an example explains the concrete mode of this invention to a detail, this invention is not limited by the following examples unless the summary is exceeded.

[Production of positive electrode] positive electrode 90 % of the weight ($LiCoO_2$) of cobalt acid lithiums as positive active material, 5 % of the weight of acetylene black as an electric conduction agent and 5 % of the weight (PVdF) of polyvinylidene fluorides as a binder are mixed in N-methyl pyrrolidone solvent. After slurring, it applied to one side of 20-micrometer aluminum foil, and dried, and what was further rolled out with the press machine was pierced and produced to punching punch with a diameter of 12mm.

[Production of negative electrode] negative electrode pierced and produced what applied to one side of the copper foil of 20-micrometer thickness, dried, and rolled them out with the press machine further after mixing and slurring 95 % of the weight (0.336nm of spacings) of graphites as a negative-electrode active material, and 5 % of the weight (PVdF) of polyvinylidene fluorides of a binder in N-methyl pyrrolidone solvent for the diameter of 12mm.

In the dry box of [assembly of cell] argon atmosphere, CR2032 mold coin cel was used and the lithium secondary battery was produced. That is, after having added the electrolytic solution after having placed the negative electrode after having placed the positive electrode on the positive-electrode can, placing the 25-micrometer porous polyethylene

film as a separator on it and pressing down with the gasket made from polypropylene, and placing the spacer for thickness adjustment, and making it sink in enough in a cell, the negative-electrode can was carried and the cell was obturated. In addition, it considered as the design from which the capacity of a cell is set to charge upper limit 4.2V in an example and the example of a comparison, and is set to about 4.0 mAh(s) by discharge minimum 3.0V.

[0032] Under the present circumstances, since the range from which the lithium ion emitted from a positive electrode in the anticipated-use upper limit electrical potential difference of a rechargeable battery does not start a deposit of a lithium metal on the negative electrode which counters was desirable, as for the ratio of weight [of positive active material] W (c), and weight [of a negative-electrode active material] W (a), that weight was determined so that the capacity factor Rq of a negative electrode and a positive electrode might be set to 1.1 <=Rq<=1.2. in addition, the capacity factor Rq -- Q(a) W[x] (a)/{Q(c) xW (c)} -- it came out and asked. Electric capacity per weight of the negative-electrode active material which can carry out occlusion of the lithium to the maximum was made into Q(a) mAh/g, without Q(c) mAh/g and a lithium metal depositing the electric capacity per [under the conditions corresponding to the initial charge conditions of a cell] weight of positive active material here. The positive electrode or the negative electrode was used for the operation pole, they used the lithium metal for the counter electrode, and Q (c) and Q (a) constructed and measured the trial cel through the separator in the same electrolytic solution as the time of assembling the above-mentioned cell. That is, it asked as the capacity which a positive electrode can charge (emission of the lithium ion from a positive electrode), and a capacity in which a negative electrode can discharge (occlusion of the lithium ion to a negative electrode) with the lowest possible current density to the upper limit potential of the positive electrode corresponding to the initial charge conditions of the target fuel cell subsystem, or the minimum potential of a negative electrode.

evaluation of [evaluation of cell] cell -- the initial charge and discharge (capacity check) of (1) -- subsequently -- (2) full charge actuation -- it carried out in order of (3) overcharge trial ** further.

[0033] In initial charge and discharge (capacity check), it charged with the constant current constant voltage anodizing process of 1C (4.0mA) and 4.2V upper limit. The cut of charge was considered as the time of a current value reaching 0.05mA. Constant current performed discharge to 3.0V by 0.2C. Full charge actuation was charged with the constant current constant voltage anodizing process (0.05mA cut) of 4.2V upper limit.

[0034] The overcharge trial was considered as 4.99 V cuts or 3hr cut (it cuts in the direction which reached the either point) by 1C. As an index which looks at the superiority or inferiority of the overcharge prevention effectiveness, the coin cel after overcharge was disassembled and the value which carried out the quantum of the Li which remains in a positive electrode by elemental analysis was used as overcharge depth. When the positive-electrode presentation after a overcharge trial is expressed as $LixCoO2$, overcharge will not progress but the overcharge prevention effectiveness will be so high that x (the amount of positive-electrode Li survival) is large.

[0035] Here, x (the amount of positive-electrode Li survival) was calculated from the number ratio of mols of Co in the positive electrode for which it asked by elemental analysis (ICP AEM), and net Li. in addition, the mol of net Li -- the analysis with the same number -- Lynn in a positive electrode -- what also performs the quantum of (P) and depends this on $LiPF_6$ -- carrying out -- the total in a positive electrode -- it deducted and asked for Li mol number equivalent to $LiPF_6$ from Li mol number.

As the example 1 electrolytic solution, what added dimethyl malonate by 2% of the weight of concentration as an additive was used for the electrolytic solution made to dissolve a hexa fluorophosphoric acid lithium ($LiPF_6$) in the mixed solvent of the volume ratio 3:7 of ethylene carbonate (EC) and diethyl carbonate (DEC) by the concentration of one mol/l.

[0036] Evaluation of the lithium secondary battery manufactured by said approach and Li analysis in the electrode which disassembles the cell after overcharge were performed. A result is shown in Table -1.

Evaluation of a lithium secondary battery and Li analysis in the electrode which disassembles the cell after overcharge were similarly performed except having added the diethyl malonate instead of the dimethyl malonate added in example 2 example 1. A result is shown in Table -1.

Evaluation of a lithium secondary battery and Li analysis in the electrode which disassembles the cell after overcharge were similarly performed except having added diethyl fumarate instead of the dimethyl malonate added in example 3 example 1. A result is shown in Table -1.

Evaluation of a lithium secondary battery and Li analysis in the electrode which disassembles the cell after overcharge were similarly performed except having not added an additive in example of comparison 1 example 1. A result is shown in Table -1.

Evaluation of a lithium secondary battery and Li analysis in the electrode which disassembles the cell after overcharge were similarly performed except having added the dibenzofuran instead of the dimethyl malonate added in example of

comparison 2 example 1. A result is shown in Table -1. In addition, electrical-potential-difference vibration considered to be based on a short circuit at the time of overcharge was observed, and the apparent amount of overcharge currents became large.
Evaluation of a lithium secondary battery and Li analysis in the electrode which disassembles the cell after overcharge were similarly performed except having added diethyl succinate instead of the dimethyl malonate added in example of comparison 3 example 1. A result is shown in Table -1.
[0037]
[Table 1]

表－1

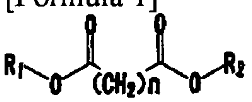
	添加剤	過充電試験 過充電電流量 (見掛け)	過充電深度 x in $LixCoO_2$	備考
実施例1	マロン酸 ジメチル	99.8 mAh/g	0.505	
実施例2	マロン酸 ジエチル	100.0 mAh/g	0.477	
実施例3	フマル酸 ジエチル	96.7 mAh/g	0.477	
比較例1	なし	81.2mAh/g	0.163	
比較例2	ジベンゾ フラン	327.8mAh/g	0.231	短絡 あり
比較例3	コハク酸 ジエチル	95.7mAh/g	0.138	

[0038] From Table -1, by adding dicarboxylic acid diester shows that the omission of Li from the positive electrode at the time of overcharge is pressed down (the value of x when expressing with LixCoO2 is large), and the safety at the time of overcharge improves. In addition, the big difference was not looked at by cell properties, such as a capacity maintenance factor after initial discharge capacity and 5 cycles, with the lithium secondary battery created in the example, and the lithium secondary battery created in the example of a comparison.
[0039]
[Effect of the Invention] According to this invention, the electrolytic solution which can raise various kinds of cell properties, such as a cycle property, a rate property, and capacity, can be offered. Especially, the electrolytic solution which can raise the safety at the time of overcharge can be offered by the new overcharge inhibitor.
[0040] Moreover, according to this invention, the cell which improved various kinds of cell properties, such as a cycle property, a rate property, and capacity, can be offered. Especially, the cell which raised the safety at the time of overcharge can be offered by the new overcharge inhibitor.

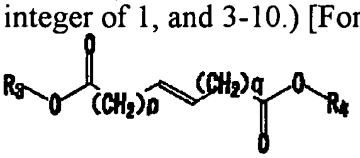
[Translation done.]

CLAIMS

[Claim(s)]
[Claim 1] The electrolytic solution characterized by containing dicarboxylic acid diester (however, oxalic acid diester and succinic-acid diester being removed) or its derivative at 0.1 - 5% of the weight of a rate to the above-mentioned solvent in the electrolytic solution which comes to dissolve lithium salt in the solvent which makes a subject at least one sort of nonaqueous solvents chosen from the group which consists of a carbonate, the ether, and lactone.
[Claim 2] The electrolytic solution according to claim 1 by which dicarboxylic acid diester is expressed with a general formula (1) or (2).
[Formula 1]


(1)

(R1 and R2 express the alkyl group or halogenation alkyl group of carbon numbers 1-10 among a formula, and n is the integer of 1, and 3-10.) [Formula 2]


(2)

(R3 and R4 express the alkyl group or halogenation alkyl group of carbon numbers 1-10 among a formula, and p and q are the integers of 0-5, respectively, and are 0 <=p+q<=10.) [Claim 3] The electrolytic solution according to claim 2 whose dicarboxylic acid diester is what is chosen from the group which consists of malonic-acid diester, diester maleate, and fumarate diester.
[Claim 4] The electrolytic solution according to claim 3 whose malonic-acid diester is what is chosen from the group which consists of dimethyl malonate, a diethyl malonate, malonic-acid dipropyl, dibutyl malonate, a malonic-acid screw (fluoro methyl), a malonic-acid screw (difluoromethyl), and a malonic-acid screw (trifluoromethyl).
[Claim 5] The electrolytic solution according to claim 3 which is what is chosen from the group which diester maleate becomes from maleic-acid dimethyl, a diethyl maleate, maleic-acid dipropyl, dibutyl maleate, a maleic-acid screw (fluoro methyl), a maleic-acid screw (difluoromethyl), and a maleic-acid screw (trifluoromethyl).
[Claim 6] The electrolytic solution according to claim 3 which is what is chosen from the group which fumarate diester becomes from dimethyl fumarate, diethyl fumarate, fumaric-acid dipropyl, fumaric-acid dibutyl, a fumaric-acid screw (fluoro methyl), a fumaric-acid screw (difluoromethyl), and a fumaric-acid screw (trifluoromethyl).
[Claim 7] The rechargeable battery characterized by having the electrolytic solution of any one publication of claim 1-6, a positive electrode, and a negative electrode.
[Claim 8] The rechargeable battery according to claim 7 with which a positive electrode contains a lithium transition-metals multiple oxide.
[Claim 9] The rechargeable battery according to claim 7 or 8 with which a negative electrode contains a carbonaceous object.

[Translation done.]